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ON THE ACTIVITY SEQUENCE OF COLD-WORKED METAL CATALYSTS FOR THE HYDROGENATION OF ETHYLENE

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Changes in the catalytic activity of cold-worked metals (Pt, Pd, Ni, and Fe) due to annealing were studied for the hydrogenation of ethylene. From a comparison between the relative activities of these metals, it was found that the findings of Beeck and *et al.* are not a complete answer to the problem of the activity sequence of metals.

Introduction

Many studies have been made since Beeck first proposed the problem of the activity sequence of metals for the hydrogenation of ethylene[1~5]. These have shown that the catalytic activities of metals can be related to their bulk electronic properties and crystal parameters. However, it has been considered that these results are not necessarily a complete answer to the catalytic activity of transition metals. Thomas indicated recently that these attempts of the last twenty years have been largely unsuccessful[6]. It is generally known that the catalytic properties of a metal are greatly influenced by the pretreatments, such as cold-working, annealing[7~10], ion-bombardment[11, 12] and quenching[13, 14]. Recent studies have shown that these changes in activity appear to be due to the nature and concentration of lattice defects as active sites which can be produced or removed by the pretreatments. The present author suggested that for the decomposition of formic acid the meaning of the comparison of the catalytic activity between different metals is doubtful and this problem can not be solved exactly without considerations for lattice defects as active sites of catalysts[15]. It is the purpose of this work to obtain

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the changes in activity of cold-worked metals (Pt, Pd, Ni and Fe) during annealing for the hydrogenation of ethylene and to make the meaning of activity sequence clearer.

Experimentals

In order to remove the oxide layer and other impurities, metal wires (99.9% or higher purity) were well annealed in hydrogen at 900°C and were rolled to a constant degree (about 80% compression) at room temperature, and then were annealed again in hydrogen for 1 hr at various temperatures. Using these samples, the catalytic activities were measured as a function of annealing temperature. In particular, Ni and Fe catalysts were annealed at 200°C in hydrogen for at least 2 hr before experiments were begun. Hydrogen made by electrolysis was purified by passing through a palladium thimble. Ethylene obtained from Takachiho Co. Ltd., was purified by repeated freezing and vacuum distillation. A mixture of ethylene and hydrogen, 1 : 1 molar ratio, was used for the reaction at the total pressure of 100 Torr. The rate of reaction was measured by a static method at 100°C. The samples of the apparent surface area 15–100 cm^2 were used as the catalyst depending upon their activities. To determine the recovery temperatures (that is, disappearance temperature of lattice defects) of these cold-worked metals during annealing, the measurements of thermoelectric power and hardness were made by the method previously described[16].

Results and Discussion

Fig. 1 shows a typical result obtained in these experiments.

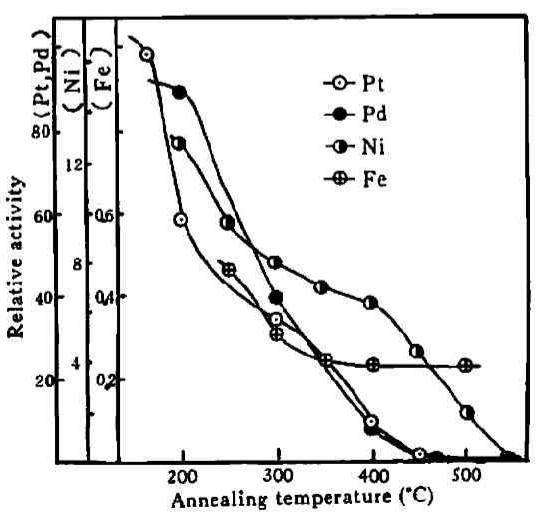

Fig. 1. The relative activities of cold-worked metals as a function of annealing temperature (reaction temperature: 100°C)

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The recovery temperatures of these metals are summarized in Table 1.

Table 1. Recovery temperature of cold-worked metals

metal	stage I (Tv)	stage II (Td)
Pt	150°C~300°C	350°C~500°C
Pd	200°C~400°C	
Ni	200°C~300°C	400°C~600°C
Fe	~200°C	250°C~500°C

The two stages, Tv and Td, are attributed to the disappearance of point defects, and the rearrangement and disappearance of dislocations produced by cold-working, respectively[8,15]. By comparing the result of Fig. 1 with that of Table 1, it is seen that the marked decrease in the activity of each metal occurs during annealing at the temperature ranges which correspond to Tv and Td. In the case of Pd, no distinction between Tv and Td is observable and only continuous decrease in activity occurs in the recovery range 200°–400°C. Eckell showed an decrease in activity of cold-worked Ni on annealing in the range 200°–300°C, while in the present result the sudden decrease occurs at the two ranges, Tv and Td. This difference is difficult to explain, but it may presumably result from the difference in the nature and the degree of cold-working, and the existence of different impurities in the samples. It may be frequently considered that the possible reasons for affecting the catalytic activity during annealing are the decrease in the surface area and decrease in the extent of active lattice planes at the surface. As discussed in the previous papers[8,15], these factors do not seem to account for the significant decrease in the activity in the restricted range of annealing. Therefore, we may conclude that the presence of lattice defects at the surface plays an important role in governing the catalytic activity of these metals. Beeck[1], and Schuit and Reijen[3] found that under the conditions of their experiments the order for the activity of metals (evaporated films and supported metals) in the hydrogenation of ethylene is given by Pd>Pt>Ni>Fe. Many studies have shown that for a number of reactions involving hydrogen either alone or with hydrocarbons this order is probably real but in some cases is only approximate due to the different preparations of catalysts[4]. The present results indicate that the activity sequence of cold-worked metals agrees nearly with the results of Beeck, *et al.* in the range of low annealing temperatures but the differences in the activity disappear after annealing at temperatures above Td. It is also suggested that the contribution of the ideal surface (which is free from lattice defects) to the activity is almost negligible and the application of this sequence to these metals is restricted to the catalysts involving many defects as active sites.

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